KINETIC STUDIES OF GAS EVOLUTION DURING PYROLYSIS OF SUBBITUMINOUS COAL[*]

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INTRODUCTION

The Lawrence Livermore Laboratory is currently developing a method for in-situ gasification of subbituminous western coals (1,2). One of the most important unresolved questions relates to the amount and type of products obtained during the pyrolysis phase. Wyoming subbituminous coal loses about 40 to 50% of its dry weight during pyrolysis, generating low-molecular-weight gases, light hydrocarbons, and heavy tars. Since such a large percentage of the coal can be removed in the form of pyrolysis products (many of which have a high heating value), the pyrolysis process must be well understood if we are to model in-situ gasification properly.

Unfortunately, the literature contains little quantitative information on subbituminous coal pyrolysis between 383 and 1273 K (110-1000°C). With this in mind, we have carried out our study of Roland seam (Wyodak mine[†]) subbituminous coal. This report describes our analysis of the major gaseous pyrolysis products (H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, and C_2H_4). These gases account for approximately 25% of the weight of the original coal. The quantity of each gas and the temperature range of evolution were determined. Also, the effective kinetics for the evolution of each species were evaluated using nonisothermal kinetic methods. Effective kinetic parameters are valuable for modeling purposes since they can accurately describe the macroscopic pyrolysis process.

Since coal is such a heterogeneous mixture of compounds, it is only possible to relate macroscopic effective kinetics indirectly to actual specific microscopic chemical and physical processes. Therefore, the results reported here are only generally correlated to the known chemistry of coal, but they provide a good physical picture of the chemical process that may occur during pyrolysis.

EXPERIMENTAL

A 50-g sample was used in the experiments. Sample preparation procedure is described elsewhere (3). Table 1 gives a standard analysis of the coal. Particle diameter distribution was from 1.68 to 3.35 mm. All samples were water-saturated, then dried in vacuum at 383 K (110°C) for 4 h. Following drying, the sample were immediately pyrolyzed. At no time was air allowed to contact the dry samples.

The details of the apparatus and procedures are described elsewhere (3). The pyrolysis apparatus consisted of a flow control unit, a reactor, and a sampling system.

The flow control unit provided a constant sweep (±1%) of Ar carrier gas through the system. Thus, we could obtain by mass spectroscopy a quantitative measure of the gaseous product composition relative to the constant background flow.

The furnace, which enclosed the reactor, was programmed to increase the temperature linearly with time (3.33°C/min). The coal sample was placed in a basket and positioned at the center of the reactor (and furnace) atop a mass of ceramic balls. The ceramic balls preheated the carrier gas to the reactor temperature. A thermocouple at the center of the coal sample monitored the temperature of the pyrolysis reaction zone.

METHOD OF KINETIC ANALYSIS

We have used nonisothermal methods to obtain the gas evolution kinetics. These methods have been described by van Heek et al. (4), who show that for a constant heating rate ($dT/dt = C$), the rate of gas evolution for a first-order reaction is given as

$$\frac{dV}{dt} = \frac{AV_\infty}{C} \exp\left(\frac{-E}{RT} - \frac{ART^2}{CE} e^{-E/RT}\right) , \qquad 1)$$

where E is the activation energy, A is the kinetic frequency factor, C is the heating rate and V_∞ is the total volume of gas evolved.

The rate of gas evolution (dV/dT) for a given costant heating rate is determined experimentally. Knowing the total volume of the material evolved, one can fit Equation 1 to the experimental results and obtain E and A. The closeness of the fit is a good indication of the validity of the assumed reaction order.

As noted in the introduction, coal is such a complicated heterogeneous mixture of different organic and inorganic compounds that the reported pyrolysis kinetics are undoubtedly an average for a vast number of different reactions that give the same product. For this reason, the activation energy and frequency factor for a particular gas evolution process are only "effective" values for the whole process.

RESULTS AND DISCUSSION

Figure 1 gives the experimentally observed gas evolution curves for the major coal pyrolysis gases: H_2, CO_2, CO, CH_4, C_2H_6, C_3H_8, and C_2H_4. These curves were obtained using a heating ramp of 3.33 K/min (3.33°C/min) between 383 and 1273 K (110°C–1000°C).

The concentrations of product gases were normalized to that of the constant-flow Ar carrier gas. Integration of the evolution envelopes provides the total volume of each gas given off during pyrolysis (Table 2).

Hydrogen evolution

Figure la and Table 2 reveal that H_2 is the major pyrolysis gas. It occurs at twice the mole concentration of any other gas and represents about 40% of the total gas evolved.

Using Equation 1, one can evaluate the activation energy and kinetic frequency factor for pyrolytic H_2 evolution by assuming that it is a first-order process. By numerically fitting Equation 1 to the experimental points in Figure la using a standard computer code (5), one can calculate an effective activation energy of 22.3 kcal/mole and a frequency factor of 1.2×10^3 min^{-1} for dehydrogenation. Figure 2a reveals the closeness of this fit to the experimental data. The activation energy and the frequency factor are the only variable parameters in the code. From the closeness of the computer fit, it appears that H_2 evolution is adequately described as a first-order process.

The observed activation energy for H_2 evolution is unusually low for the temperature at which it took place. The activation energy for a typical C-H bond-breaking process is about 101 kcal/mole. Berkowitz and den Hertog (6) report activation energies of 8 to 15 kcal/mole for pyrolytic dehydrogenation of other coal types between 873 and 1073 K (600-800°C), and their low values are in fair agreement with the results reported here for Roland seam coal. It would appear therefore that the simple bond-breaking picture is inadequate.

It is well known that H_2 evolution in coal results from the fusion of aromatic ring structures (lamellae) in the coal matrix. This reaction can be schematically represented as

$$Ar - H + Ar' - H \rightarrow Ar' - Ar + H_2,$$
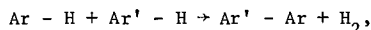
where Ar and Ar' represent particular lamallae structures containing n and n' aromatic ring units each (e.g., pyrene and phenantherene). Berkowitz and den Hertog (6) proposed that the diffusion of two lamellae into some configuration where reaction becomes possible is the rate-determining step. The activation energy observed for H_2 emission would then be a measure of the activation energy associated with the diffusion of the lamellae units.

Since char is such a heterogeneous mixture of materials, it is also possible that H_2 emission occurs from a number of chemically nonequivalent sites, each with its own activation energy. If this is the case, the experimentally observed dehydrogenation curve represents the sum total of H_2 from many different sites. Thus the activation energy for H_2 release from each site sould be quite high (>>20 kcal/mole), and yet the curve (Fig. 2a) would give the appearance of a low activation energy overall. The observed temperature dependence of the total H_2 release (7,8) gives support to this view. As temperature increases, the H_2 release increases, although at each temperature, dehydrogenation goes essentially to completion. This indicates that a number of different H_2 formation reactions take place, each occuring at a different temperature.

Carbon oxides

Carbon dioxide. Carbon dioxide is the first pyrolysis gas to be relased in appreciable quantities (Fig. 1b). A trace of CO_2 appears at about 523 K (250°C), goes through maxima at 793 K (470°C) and about 923 K (650°C), and then eventually declines to zero at 1123 K (850°C). The twin peaks seem to indicate CO_2 emission from at least two distinct sources. The first peak may be due in large part to carboxylic acid (COOH) decomposition; the second peak probably results from carbonate decomposition in the minerals. Fitting Equation 1 to the observed evolution curve gives the values of the effective activation energies and frequency factors (Table 2). Figure 2b shows the closeness of the calculated fit.

Blom (9) reported the distribution of oxygen functional groups in vitrains of various C and O content. For a vitrain of about 18 wt% O_2 and 73 wt% C, dry and mineral-matter free (a composition similar to that of Roland seam coal as described in Table 1), the amount of O as COOH is about 3 to 4 wt% (i.e., about 17 to 22% of the total O). The amount of O as COOH needed to produce the first peak in Fig. 2b would be ∿4.4 wt% of the coal (i.e., 25% of the total O). This approximation is only slightly higher than Blom's results.

The second CO_2 peak occurs at a temperature in the range of carbonate decomposition reactions for a number of minerals. O'Gorman and Walker (10) have carried out an extensive study of mineral matter in U.S. coals. Their work includes data for the original mineral (unheated) and final ash samples from 57 different coals. Samples of Wyoming subbituminous coal with an ash composition similar to Roland seam coal (in terms of constituent oxides) contained ankerite.[*] Calcite, argonite, dolomite, and siderite were not detected. Thermal analysis work by Kulp et al. (11) on ankerite shows that the principal carbonate decomposition occurs at about 923 to 973 K (650-700°C). This is in reasonable agreement with the observed second CO_2 peak in Fig. 2b.

Carbon monoxide. The evolution of CO is similar to that for CO_2 in that two peaks are observed. The first peak is at about 773 to 823 K (500-550°C) and the second is at 973 to 1023 K (700-750°C). A numerical fit to the data in Fig. 1b gives the effective kinetic parameters reported in Table 2. These parameters give an accurate representation of the process, as can be seen from the closeness of the fit in Fig. 2c.

The evolution of CO during coal pyrolysis has been attributed to several sources, primarily ether linkages, ketone groups, and heterocyclics. Fitzgerald and van Krevelen (12) suggest that CO formed at low temperatures [T < 773 K (T < 500°C)] arises from decomposition of ether links and carbonyl groups and that CO at high temperatures [T > 773 K (T > 500°C)] results from degradation of heterocyclic compounds.

However, due to the presence of CO_2 in the pyrolysis gas at high temperatures, some of the CO may be a product of the well-known Boudouard reaction:

$$CO_2 + C_{(s)} \rightarrow 2CO.$$

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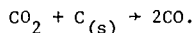
[*] $Ca(Mg,Fe)(CO_3)_2$.

Yergey and Lampe (13) studied the mechanism of this reaction to determine if CO evolution is a two-step process or a simultaneous release of both CO molecules. Using nonisothermal kinetic methods, they show that oxygenated C resulting from CO_2 reaction (at 1% in flowing Ar) evolves simultaneously (desorbs) at a peak maximum of about 600 K (330°C) for pure C and about 700 K (430°C) for coke from bituminous coal. They also report an activation energy 17.5 kcal/mole for CO desorption from bituminous coke. Probably a portion of the CO evolved in the region of 700 K (430°C) is a result of desorption.

Taylor and Bowen (14) investigated the kinetics for CO_2 reaction with char from Roland seam coal at temperatures above the CO desorption regime (in the region of about 900-1050 K). They report an appreciable rate for the CO_2-char reaction at the higher temperatures. For example, at 1023 K (750°C) and 1 atm CO_2, 25 wt% of the char undergoes reaction in 30 min. So, during pyrolysis at high temperatures (about 1000 K), it is reasonable to expect some CO production from char reaction with evolved CO_2 (particularly CO_2 that may be generated from mineral decomposition at these high temperatures).

Major Hydrocarbon Gases

Ethane, propane, and ethylene. Based on the total amount of pyrolysis gas evolved, C_2H_6, C_3H_8, and C_2H_4 are only minor constituents. However, because their heats of combustion far exceed those of other gas components, they have a large effect on the Btu value of the pyrolysis product gas even at low concentrations (Table 3). The combined concentration of C_2H_6, C_3H_8, and C_2H_4 is only 3.56% of the evolved gas, but these gases provide 14.4% of the total gas heat of combustion.

The pyrolysis peak maxima for the above three gas hydrocarbons are nearly equivalent; i.e., 783 to 793 K (510-520°C). Barker (15) measured the peak maximum for the combined C_1 to C_{10} hydrocarbon release from a number of vitrinites. A value of 753 K (480°C) was reported for the broad peak observed for Roland-Smith (Wyodak) vitrinites (70.2% C, dry, ash-free). The release of condensible liquid hydrocarbons goes through a maximum of 673 to 723 K (400-450°C) (16).

Table 2 gives the kinetic parameters (calculated using Equation 1) for the release of the three gas hydrocarbons. Figure 2 shows a typical fit for C_2H_6. Van Heek and Jüntgen (4) report an activation energy of about 41 or 42 kcal/mole for C_2H_6 evolution from hard coal. As expected, this value is somewhat higher than the one reported here, since the temperature and activation energy of hydrocarbon release increase with rank.

The source of these light hydrocarbons is thought to be aliphatic side chain groupings and inter-lamellae linkages cracked at higher temperatures. Work on model compounds by Depp et al., shows that methylene and ethane linkages, in particular, are quite weak (17).

98

A review by Tingey and Morrey (18) states that the amount of C present as aliphatic material is generally high for low-rank coals. The major alkane side groupings are methyl, ethyl, and propyl with small amounts of butyl. Alkane units of Cn, n > 4 are rare. On the other hand, the concentration of methyl groups is by far the largest and is usually reported to be greater than one pre-aromatic lamellae (18).

Methane

In terms of heating value, CH_4 is the most important pyrolysis product. It accounts for about half the total heat of combustion of the pyrolysis gases (Table 3). Methane evolves over a rather large temperature range (Fig. 1b). The original sharp increase in CH_4 production occurs at the same temperature as observed for the other light hydrocarbons (Fig. 1c). However, the CH_4 peak tails off slowly at high temperatures and does not reach essentially zero until 1173 K (900°C).

It appears that CH_4 production in the 770 K (500°C) region results from dealkylation, the general mechanism proposed to produce other light hydrocarbons. At higher temperatures [T > 820 K (T > 550°C)], CH_4 production is undoubtedly due to another (or many other) reactions. Fitzgerald and van Krevelen suggest that, at these higher temperatures, CH_4 is produced from char autohydrogenation reactions (12). Due to the high-temperature tail on the CH_4 curve, it is impossible to represent gas evolution accurately using a single first-order decomposition mechanism. For this reason, a sum of three curves was used. This is the minimum number that will give a close fit on the experimental data. For modeling purposes, it is reasonable to use more than one curve to fit the data, since accurate representation of the overall process is important. However, on a physical basis, it is difficult to identify the source of each peak.

As discussed above, the first sharp rise in CH_4 evolution (at about 770 K) probably results from dealkylation. Since the kinetic parameters for evolution of C_2H_6, C_3H_8, and C_2H_4 are nearly equivalent, the activation energy for the initial production of CH_4 would be expected to be 30 to 35 kcal/mole. By using an activation energy of 31.0 kcal/mole for the first peak, one can accurately represent the initial rise in the CH_4 evolution curve. This agrees with the expected result.

SUMMARY AND CONCLUSIONS

Gas evolution during pyrolysis of Roland seam (Wyodak mine) subbituminous coal was investigated from 383 to 1273 K (110-1000°C) in an inert gas (Ar) environment. The effective kinetic parameters (activation energy and frequency factor) for each major gas evolved were determined using nonisothermal kinetic methods. Effective kinetics provide valuable input for modeling processes involving coal pyrolysis (e.g., in situ coal gasification). Table 2 summarizes these kinetic results.

From the experimental results, a quantitative measure of each major gas evolved was also obtained. The temperature region and temperature maximum for the pyrolytic release of each gas were determined.

The observed gas evolution processes generally correlated with decomposition of known chemical structures in coal. This provided a good physical picture of the possible chemical reactions during pyrolysis.

ACKNOWLEDGMENTS

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Table 1. Standard chemical analysis of Roland seam coal.

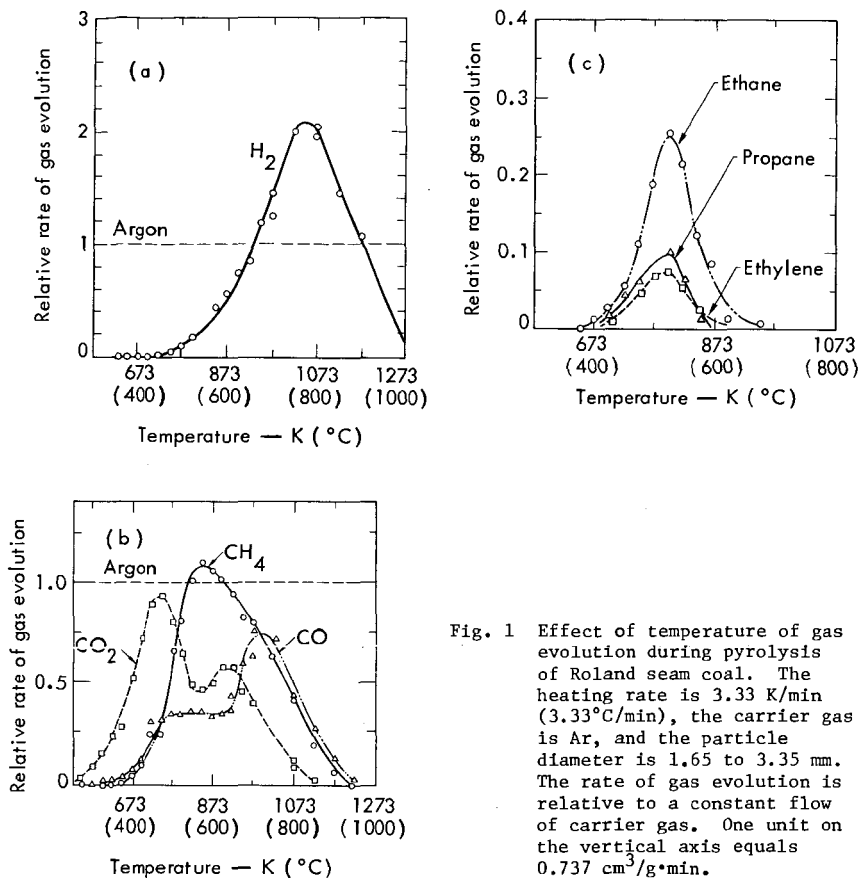| Characteristic	As received	Dry sample
Ultimate analysis		
Moisture	34.67%	—
Carbon	43.61	66.76%
Hydrogen	3.44	5.25
Nitrogen	0.73	1.11
Chlorine	0.01	0.01
Sulfur	0.48	0.74
Ash	5.96	9.13
Oxygen (by difference)	11.10	16.99

Fig. 1 Effect of temperature of gas evolution during pyrolysis of Roland seam coal. The heating rate is 3.33 K/min (3.33°C/min), the carrier gas is Ar, and the particle diameter is 1.65 to 3.35 mm. The rate of gas evolution is relative to a constant flow of carrier gas. One unit on the vertical axis equals 0.737 cm^3/g·min.
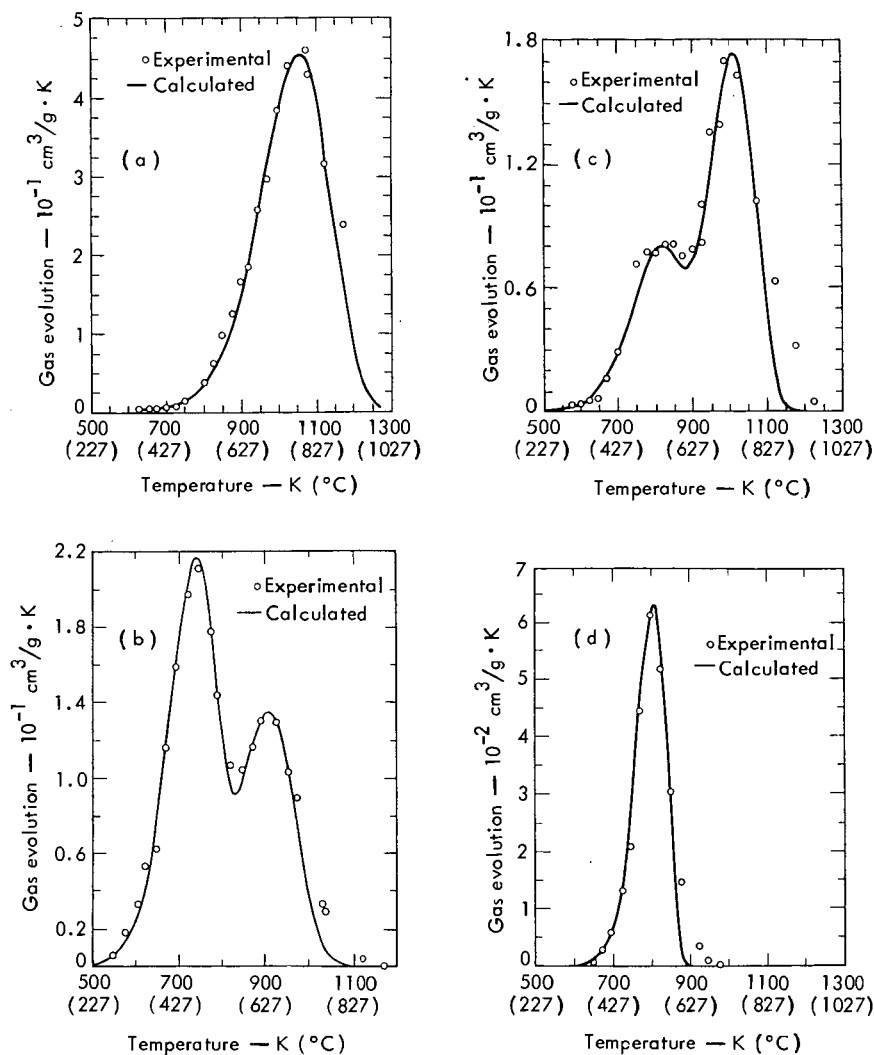
Fig. 2 Numerical fit of Equation 1 to experimental data for gaseous
evolution of (a) H_2, (b) CO_2, (c) CO, and (d) C_2H_6. Since the
time-temperature scales are coupled, the rate is in units of
$cm^3/g \cdot K$. To convert to time units, multiply by the heating rate
of 3.33 K/min.